



Short communication

Highly enhanced capacitance of MgO-templated mesoporous carbons in low temperature ionic liquids



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HIGHLIGHTS

- The present work reports a low temperature operation of EDLC with ionic liquid electrolytes.
- MgO-templated mesoporous carbons show much higher capacitance retention than activated carbons below 0 °C.
- Mesopores of the carbon provide easily accessible pathways for the ions.

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ABSTRACT

MgO-templated mesoporous carbons with high specific surface areas were employed for the electrode materials of electric double layer capacitors (EDLCs) in low temperature ionic liquids. The mesoporous carbons exhibit strongly enhanced capacitance in ionic liquids at 20 to −40 °C compared to conventional activated carbons. Mesopores in the carbon electrodes provide a smooth pathway for the ions, and minimize the temperature influence on the diffusion resistance of the ions. Thus, this paper confirms that mesoporous carbons work as electrode materials to achieve highly enhanced capacitances below 0 °C in ionic liquids, which leads to wide ranging applications of EDLC devices.

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1. Introduction

Electric double layer capacitors (EDLCs) based on carbon materials have a potential to become high power devices for automotive applications because of the high power density and long life [1–3]. Organic solutions such as propylene carbonate and acetonitrile are typically used with quaternary ammonium salts as electrolytes of EDLCs [4–6]. For the applications to electric vehicles in various environments all over the world, operation at a wide range of temperatures from −30 to +60 °C is required [7]. Several researchers reported the temperature influence on the performances of EDLCs using propylene carbonate or acetonitrile [8–11]. It is concluded in these literatures that the temperature influence on the diffusion resistance of the ions is much more prominent for propylene carbonate than for acetonitrile, and hence acetonitrile based electrolyte is prospective for low temperature operation. However, a major drawback of acetonitrile is a safety issue such as

volatility and flammability. Ionic liquids are attractive electrolytes which can be alternative to the conventional organic electrolytes because of negligible vapor pressures, low-flammability, and high electrochemical stability [12–15]. In addition to safety features compared to organic electrolytes, ionic liquids enable high voltage operation of EDLCs leading to high energy densities. Due to these properties, many researchers explored the performances of EDLCs using ionic liquids at room temperature [16–22]. In spite of considerable efforts, still the use of ionic liquids is limited because of the low conductivity. Moreover, there are few reports on the low temperature operation of ionic liquid EDLCs. Recently, Senda et al. used fluorohydrogenate ionic liquids which has relatively high conductivities, and exhibited good performances at −40 °C using conventional activated carbons [23]. In addition to such an electrolyte engineering approach, controlling pore structures of carbon materials is effective to decrease the diffusion resistance of the ions that dominantly control the cell resistance at low temperatures. Very recently, we have reported the effect of mesopores in the MgO-templated mesoporous carbons on capacitor performances at low temperatures in 1 M TEABF₄/PC electrolyte [24]. We considered that dominant mesopores in the carbon electrode leads to the low

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internal resistance with smooth migration of the ions and enables the low temperature operation of EDLCs. However, the mesoporous carbons have not been investigated in low temperature ionic liquids. In the present study, we examine the low temperature operation of EDLCs using the MgO-templated mesoporous carbon electrode in the following ionic liquids: BMIBF₄, HMIBF₄, and DEMETFSA. These ionic liquids were chosen among typically studied ionic liquids because their melting points are low enough for low-temperature operations.

2. Experimental

MgO-templated mesoporous carbons (CNovel® annealed at 900 °C, Toyo Tanso Co., Ltd.) and, for comparison, commercially available activated carbons (YP-17, Kuraray Co., Ltd., BET surface area: 1500 m g⁻¹) were employed for the active materials of the electrodes. These carbons are denoted as MPC and AC, respectively. MPC mainly possesses mesopores in contrast to AC that is dominated by micropores as the pore dimensions are summarized in Table 1 [24,25]. For the electrochemical measurement, carbon sheet electrodes composed of 80 wt% active material, 10 wt% PTFE, and 10 wt% acetylene black were used after dried overnight under vacuum at 150 °C. All the sheet electrodes were fabricated with a diameter of 10 mm and a thickness of 0.1 mm. Laminated-type cells were assembled in a two electrode configuration after carbon electrodes and separators (TF40-50, Nippon Kodoshi Co.) were impregnated with electrolytes for an hour under reduced pressure. Etched aluminum foils were used as current collectors. BMIBF₄ (1-butyl-3-methylimidazolium tetrafluoroborate), HMIBF₄ (1-hexyl-3-methylimidazolium tetrafluoroborate), and DEMETFSA [N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl) amide] purchased from Kanto Chemical Co., Inc. were used as ionic liquid electrolytes. Physicochemical properties of these ionic liquids are summarized in Table 2 [26–29]. Charge/discharge tests were carried out using a BioLogic VMP2 multi-channel galvanostat-potentiostat in a voltage range of 0 and 2.5 V with a constant current of 0.2 mA cm⁻² at 20 to –40 °C. The cell was cooled by 10 °C, and was maintained at each temperature for 10 h before electrochemical measurements.

3. Results and discussion

Charge/discharge tests were firstly carried out at 20 °C. Gravimetric discharge capacitance, *C*, was calculated by the following equation:

$$C = \frac{i}{(\Delta V / \Delta t) \cdot m} \quad (1)$$

where *i* is the discharge current, Δ*V* is the cell voltage change, Δ*t* is the discharge time, and *m* is the weight of the active materials in the two electrode (not including PTFE and acetylene black). The result at 20 °C is summarized in Table 3. Gravimetric capacitance of MPC is comparable to or higher than that of AC in all the ionic liquids. Then, the temperature was lowered by 10 °C and low temperature operation was examined. Fig. 1 shows the charge/

Table 2

Physicochemical properties of BMIBF₄, HMIBF₄, and DEMETFSA [26–29].

	Melting point/°C	Density ^a /g mL ⁻¹	Conductivity ^a /mS cm ⁻¹	Viscosity ^a /cP
BMIBF ₄	–85 [27]	1.21 [27]	3.5 [27]	180 [27]
HMIBF ₄	–82 [26]	1.08 [26]	1.8 [28]	211 [26]
DEMETFSA	(–91) [29] ^b	1.42 [29]	3.5 [29]	120 [29]

^a At room temperature.

^b Glass transition temperature. The melting point was not detected.

Table 3

Gravimetric capacitance (F g⁻¹) of MPC and AC in BMIBF₄, HMIBF₄, and DEMETFSA at 20 °C.

	BMIBF ₄	HMIBF ₄	DEMETFSA
MPC	29.8	40.4	32.0
AC	29.9	26.0	25.9

discharge curves for MPC and AC in BMIBF₄ at 20 to –40 °C. Whereas AC showed a rapid decrease of the discharge time with every decrease of temperature, MPC exhibited a gradual shortening of the time from 20 to –20 °C. Below –20 °C, temperature influence became larger even for MPC. In the same manner, the charge/discharge tests were performed in HMIBF₄ and DEMETFSA. Fig. 2 shows the capacitance retention at low temperatures in each ionic liquid. Capacitance retention was determined by eq. (2) using the discharge capacitance at each temperature, *C_T*, and the value at 20 °C, *C₂₀*.

$$\text{Capacitance retention (\%)} = \frac{C_T}{C_{20}} \times 100 \quad (2)$$

Clearly, MPC shows much better retentions than AC independently from the kind of ionic liquids. This result is attributable to existence of mesopores in the MPC electrode. MPC has a larger amount of mesopores than AC as shown in Table 1. Facilitated migration of the ions in the mesopores would suppress elevation of the diffusion resistance of the ions at low temperatures. However, the retention rapidly decreased at –40 °C for BMIBF₄ and DEMETFSA (Fig. 2(a) and (c)), and at –30 °C for HMIBF₄ (Fig. 2(b)). At these temperatures, the ion diffusion resistance of the ions in the pores would be so significant even though the pores of the carbon electrode are meso-sized. Comparing the results with the previous data of capacitance retentions for EDLCs in PC [24] (96% for AC, and 99% for MPC at –20 °C), the retention in ionic liquids (for instance, 28% for AC, and 93% for MPC at –20 °C in BMIBF₄) are lower. However, the effect of mesopores is much larger in ionic liquids than in PC. It is considered that this phenomenon is related to the ion sizes and the viscosity of electrolytes. In order to further discuss the effect of mesopores, equivalent series resistances (ESR) were determined from the IR drops in discharge curves. Fig. 3 shows the Arrhenius plots for the ESR and the corresponding activation energies calculated from the slopes. *E_{MPC}* and *E_{AC}* are activation energies for MPC and AC, respectively. This ESR is composed of several resistances originating from the bulk electrolyte, diffusion of the ions, contact between carbons and aluminum current correctors, and the carbon-electrolyte interfaces. Apparently, the slope is different between high (from 20 to 0 °C) and low (from –10 to –40 °C) temperature region. *E_{AC}* is larger at high temperatures than that at low temperatures. Because AC has dominantly micropores, the migration of the ions is hindered by the pores and the diffusion resistance of the ions in the pores is easily elevated by lowering of temperature. The insensitivity to temperature change for AC below 0 °C suggests that the ESR is controlled by other

Table 1

Pore dimensions of MPC and AC determined by N₂ adsorption [24].

	<i>S_{BET}</i> /m ² g ⁻¹	<i>V_{total}</i> /ml g ⁻¹	<i>V_{meso}</i> /ml g ⁻¹	<i>V_{micro}</i> /ml g ⁻¹
MPC	1530	2.15	1.59	0.56
AC	1453	0.80	0.14	0.66

V_{total}: calculated from adsorption amount of N₂ at *P*/*P*₀ = 0.99, *V_{meso}*: calculated by the BJH method, *V_{micro}*: difference between *V_{total}* and *V_{meso}*.

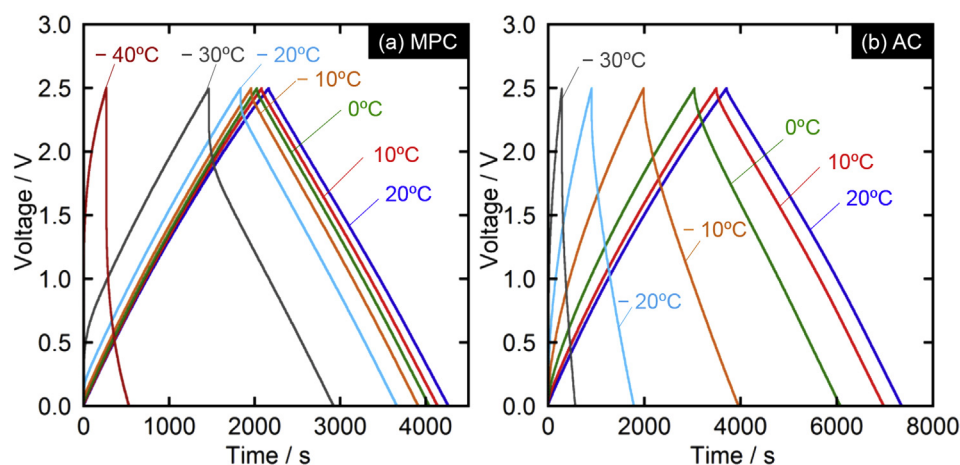


Fig. 1. Charge/discharge curves (6th cycle) at 0.2 mA cm^{-2} for (a) MPC and (b) AC in BMIBF₄. The weights of active materials are (a) 2.3 mg and (b) 4.2 mg, respectively.

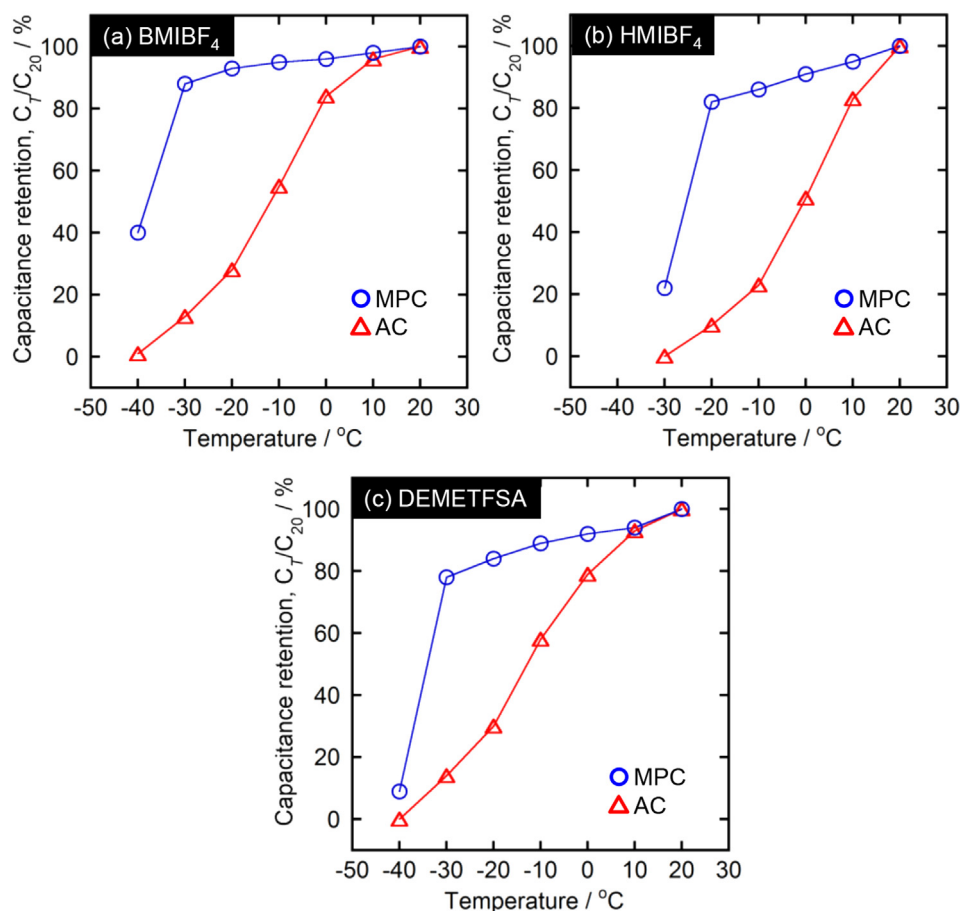


Fig. 2. Capacitance retention (C_7/C_{20}) from 20 to -40°C in reference to the capacitance at 20°C in (a) BMIBF₄ (b) HMIBF₄, and (c) DEMETFSA.

factors such as conductivity of the carbon electrodes, interfacial resistances of carbon-electrolyte and carbon-aluminum current collector, rather than the diffusion resistance of the ions in the pores. It is deduced that the diffusion resistance of the ions in the micropores rises up to a certain level around 0°C and, at lower temperatures, it does not largely depend on temperature because migration of the ions in the micropores is significantly limited. On the other hand, E_{MPC} was relatively small at the high temperature region, and became larger at the low temperature region.

Remarkable is that E_{MPC} is much lower than E_{AC} at the high temperature region ($E_{\text{MPC}} = 19$, and $E_{\text{AC}} = 63 \text{ kJ mol}^{-1}$ for BMIBF₄ as shown in Fig. 3(a)). This mild temperature dependence (low activation energy) is attributed to existence of mesopores in MPC resulting in a smooth pathway for the ions. Increase of E_{MPC} at lower temperatures indicates that mesopores cannot work effectively as a smooth pathway for the ions below 0°C . Lowering of temperature causes increasing viscosities and decreasing conductivities of ionic liquids, and therefore the diffusion resistance of the

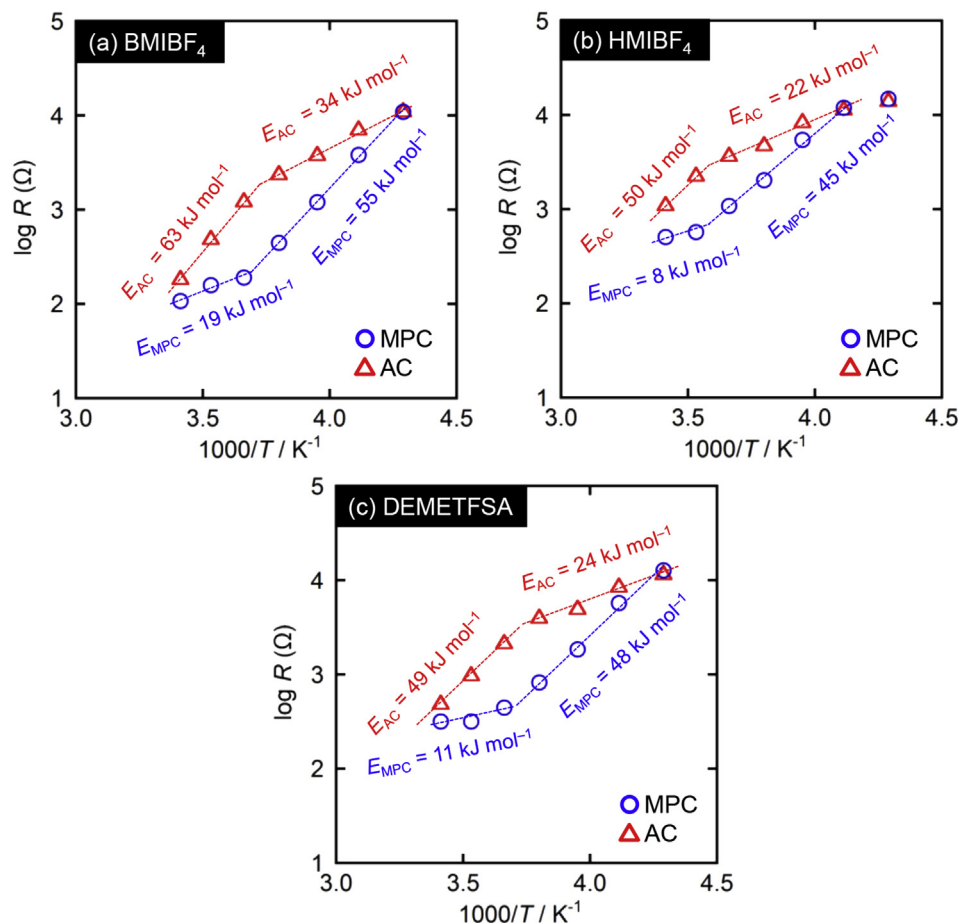


Fig. 3. Arrhenius plots for the equivalent series resistance determined from IR drops in (a) BMIBF₄ (b) HMIBF₄, and (c) DEMETFSa. Activation energies (E) were calculated from the slopes.

ions becomes more significant at lower temperatures even if the pores are meso-sized. This idea might be supported by a fact that E_{MPC} at low temperatures is comparable to E_{AC} at high temperatures ($E_{MPC} = 55$, and $E_{AC} = 63$ kJ mol⁻¹ for BMIBF₄ as shown in Fig. 3(a)). It is likely that mesopores at low temperatures make an influence on mobility of the ions as much as micropores at high temperatures. In addition, E_{MPC} and E_{AC} have similar values in each ionic liquid at the same temperature regions, indicating that the temperature influence is independent from the kinds of ionic liquids among BMIBF₄, HMIBF₄ and DEMETFSa.

4. Conclusions

The present works demonstrate the outstanding effect of mesopores on low temperature operations of EDLCs with ionic liquids. Mesopores of carbon electrodes provide a smooth pathway for the ions and minimize the elevation of the diffusion resistance at low temperatures. We believe that the EDLC performance will be further enhanced in combination of the mesoporous carbons with novel ionic liquids which has the higher conductivities and lower viscosities since it would depend on the properties of carbon electrodes as well as ionic liquids.

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References

- [1] A. Burke, J. Power Sources 91 (2000) 37–50.
- [2] M.W. Verbrugge, Supercapacitors and automotive applications, in: Proceedings Volume for the World Summit on Advanced Capacitors, Washington, DC, 2003.
- [3] A. Chu, P. Braatz, J. Power Sources 112 (2002) 236.
- [4] A.B. McEwen, S.F. McDevitt, V.R. Koch, J. Electrochem. Soc. 144 (1997) L84–L86.
- [5] B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, J. Electrochem. Soc. 146 (1999) 1687–1695.
- [6] M. Ue, K. Ida, S. Mori, J. Electrochem. Soc. 141 (1994) 2989–2995.
- [7] P. Simon, Y. Gogotsi, Nat. Mater. 7 (2008) 845.
- [8] K. Hung, C. Masarapu, T. Ko, B. Wei, J. Power Sources 193 (2009) 944–949.
- [9] R. Köts, M. Hahn, R. Gallay, J. Power Sources 154 (2006) 550–555.
- [10] P. Liu, M. Verbrugge, S. Soukiazian, J. Power Sources 156 (2006) 712–718.
- [11] M. Arulepp, L. Permann, J. Leis, A. Perkson, K. Rumma, A. Jänes, E. Lust, J. Power Sources 133 (2004) 320–328.
- [12] T. Welton, Chem. Rev. 99 (1999) 2071.
- [13] R. Hagiwara, Y. Ito, J. Fluor. Chem. 105 (2000) 221.
- [14] T. Tsuda, C.L. Hussey, Electrochem. Soc. Interface (Spring) (2007) 42.
- [15] M. Ue, M. Takeda, M. Takehara, S. Mori, J. Electrochem. Soc. 144 (1997) 2684.
- [16] T. Sato, G. Masuda, K. Takagi, Electrochim. Acta 49 (2004) 3603.
- [17] S. Shiraishi, T. Miyauchi, R. Sasaki, N. Nishina, A. Oya, R. Hagiwara, Electrochemistry 75 (2007) 619.
- [18] N. Handa, T. Sugimoto, M. Yamagata, M. Kikuta, M. Kono, M. Ishikawa, J. Power Sources 185 (2008) 1585.
- [19] R. Taniki, K. Matsumoto, T. Nohira, R. Hagiwara, J. Electrochem. Soc. 160 (2013) A734–A738.
- [20] M. Ue, M. Takeda, A. Toriumi, A. Kominato, R. Hagiwara, Y. Ito, J. Electrochem. Soc. 150 (2003) A499.
- [21] E. Frackowiak, J. Braz. Chem. Soc. 17 (2006) 1074–1082.
- [22] S. Yamazaki, T. Ito, M. Yamagata, M. Ishikawa, Electrochim. Acta 86 (2012) 294–297.

- [23] A. Senda, K. Matsumoto, T. Nohira, R. Hagiwara, J. *Power Sources* 195 (2010) 4414–4417.
- [24] Y. Soneda, M. Kodama, *Electrochemistry* 81 (2013) 845–848.
- [25] T. Morishita, T. Tsumura, M. Toyoda, J. Przepiórski, A.W. Morawski, H. Konno, M. Inagaki, *Carbon* 48 (2010) 2690.
- [26] D. Han, K.H. Row, *Molecules* 15 (2010) 2405–2426.
- [27] T. Nishida, Y. Tashiro, M. Yamamoto, J. *Fluor. Chem.* 120 (2003) 135–141.
- [28] J. Vila, L.M. Varela, O. Cabeza, *Electrochim. Acta* 52 (2007) 7413–7417.
- [29] T. Sato, G. Masuda, K. Takagi, *Electrochim. Acta* 49 (2004) 3603–3611.